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Synchronized Current Oscillations of Formic Acid Electro-oxidation in a Microchip-based Dual-Electrode Flow Cell

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Abstract

We investigate the oscillatory electro-oxidation of formic acid on platinum in a microchip-based dual-electrode cell with microfluidic flow control. The main dynamical features of current oscillations on single Pt electrode that had been observed in macro-cells are reproduced in the microfabricated electrochemical cell. In dual-electrode configuration nearly in-phase synchronized current oscillations occur when the reference/counter electrodes are placed far away from the microelectrodes. The synchronization disappears with close reference/counter electrode placements. We show that the cause for synchronization is weak albeit important, bidirectional electrical coupling between the electrodes; therefore the unidirectional mass transfer interactions are negligible. The experimental design enables the investigation of the dynamical behavior in micro-electrode arrays with well-defined control of flow of the electrolyte in a manner where the size and spacing of the electrodes can be easily varied.

Keywords

synchronization; non-linear dynamics; formic acid oxidation; microfluidics; microchip; microfabricated cell; microelectrode

1. Introduction

Electrochemical processes rely on the interaction of chemical reactions, flow of reactant and products, and electrical effects. Because of the complex nature of interactions many industrial applications require spatial and temporal characterization of electrochemical properties. For example, in fuel cells the interactions of current generating chemical reactions on multi-electrodes with fuel flow and external load can produce complex responses [1,2]; it was also shown that a proton exchange membrane fuel cell exhibits larger power in the oscillatory state than in the corresponding stationary state [3]. The electrode of interest often consists of many particles (e.g., dual electrode flow cell [4], carbon matrix Pt nanoparticles in fuel cells [1]); interaction among particles adds a further level of complexity to the spatio-temporal behavior.

The application of non-linear dynamics tools to electrochemical systems has shed light on the major mechanisms of temporal and spatial self-organization [5,6]. Negative differential resistance due to catalytic/inhibition effects and external cell control are the major components for generation of non-linear phenomena (bistability, oscillations, and stationary and oscillatory

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pattern formation) on single electrodes. Multi-electrode array configurations have been used to identify spatiotemporal phenomena in spread of corrosion [7,8], CO electro-oxidation [9], synchronization [10–18] and dynamical differentiation [19,20] of oscillators in metal dissolution systems and H₂O₂ reduction [21,22]. The cell geometry (placement and size of working, reference, and counter electrodes) greatly affects both the local dynamics through changes in solution resistance and the observed spatial patterns through global/long range electric coupling. [5]

A fundamental challenge of experimental electrode array studies is the establishment of well-defined mass transfer conditions for providing fresh electrolyte solutions to and removing the reaction products from the surface. When the number of electrodes are small (e.g., two) or local measurements are not required, rotating disks can be used. An impinging jet system was developed for the investigation of oscillations on the mass transfer limited region of dissolution of arrays of relatively large (>10) number of electrodes [23]. However, investigators have chosen electrochemical reactions under kinetic control where critical phenomena occurs at stagnant or weakly stirred conditions because of the difficulty of providing laminar flow in macro-electrode cells.

Microchip-based devices have gained considerable interest in electro-analytical applications. There are several advantages of using microchip-based systems [24–26]; these include fast analysis times (on the orders of seconds), the possibility for portability and disposability, small analyte volumes (on the order of nanoliters), and the ability to inject sample volumes as small as picoliters with microfluidics. Interdigitized electrode arrays with channel networks provide a convenient way of instrument miniaturization; for example, in microchip electrophoresis, micromolded carbon dual electrodes were used with a palladium decoupler for amperometric detection [26]. In addition, the electrode can be fabricated directly on the chip, leading to a fully integrated system. The sensitivity of electroanalytical analysis is increased, due to the increased flux towards the microelectrode surface [27] and the reduced background current of microelectrodes [28] leading to an increased coulometric efficiency. While the fluidic portion of these devices can be made in a variety of substrates, devices fabricated by soft lithography in poly(dimethylsiloxane) (PDMS) hold several unique advantages [29]. Rapid prototyping procedures can be utilized to make the initial master, greatly reducing the costs associated with making new designs. In addition, the ability to reversibly seal PDMS to a variety of substrates makes integration of the fluidic channels with the electrode network relatively straightforward [25]. Therefore, micro-chip technologies combined with microfluidics provide convenient ways to construct electrode arrays of tunable electrode sizes and spacing and to establish laminar flow of electrolytes to the electrodes.

In this paper, we explore the flexibility of a microchip based cell design with microfluidic flow control to investigate the effect of weak although important interactions among electrode particles on oscillatory dynamics. We have chosen the electro-oxidation of formic acid on Pt because (i) Pt electrodes are relatively easy to fabricate with traditional lithography and wet etching steps, (ii) the oscillatory dynamics are relatively well-understood in macro-electrode settings [30–32], and (iii) the reaction plays an important role in formic acid fuel cells. [33] We characterize the bistable/oscillatory regions under potentiostatic cell control on single electrodes of microfluidic flow cells as a function of external resistance and circuit potential. In dual-electrode setup, we investigate the effect of reference electrode position on the extent of synchronization properties of oscillations due to inter-particle interactions. Finally, we clarify the role of coupling mechanism between the oscillators and determine the relative importance of unidirectional mass transfer and bidirectional electric coupling in the proposed chip design.

2. Experimental

2.1. Schematic

A schematic of the dual-electrode microfluidic flow cell set-up is shown in Figure 1a. The electrolyte is pumped in a $120\text{ }\mu\text{m}$ (width) $\times$ $100\text{ }\mu\text{m}$ (depth) flow channel at flow rates $Q = 0.1\text{--}5\text{ }\mu\text{L/min}$ typically used in electroanalytical applications [34, 35]. For most of the experiments in this study, a flow rate of $1.5\text{ }\mu\text{L/min}$ was utilized. This corresponds to a linear velocity of 0.208 cm/s . The electrolyte flows over the front (upstream) and rear (downstream) $120\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ Pt ($0.2\text{ }\mu\text{m}$ thick) working electrodes. The two working electrodes are connected to CH Instruments 812B potentiostat through two external resistors. At the end of the flow channel there is a 3.2 mm diameter channel reservoir; the Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode (exhibiting 655 mV electrode potential vs. standard hydrogen electrode) and a 0.5 mm thick Pt wire counter electrode is placed into the center of the reservoir. All the given potentials are with reference to the Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode.

2.2. Chip fabrication

The Pt micro-electrodes were patterned by photolithography with a method similar to that used in fabricating palladium decouplers for microchip electrophoresis [26]. The Nanofabrication Facility at Stanford University was responsible for sputtering a titanium adhesion layer ($0.02\text{ }\mu\text{m}$ followed by a $0.2\text{ }\mu\text{m}$ platinum layer) on high quality, 10 cm diameter, borosilicate glass. A positive transparency (3600dpi, The Negative Image, St. Louis, MO) was created using the appropriate design drawn in Macromedia Freehand. A positive photoresist (AZ 1518) was dynamically dispensed (200 rpm) onto the plate followed by a final spin rate of 3000 rpm for 40 s. After a short $100\text{ }^{\circ}\text{C}$ bake, the transparency was laid over the resist-covered plate and exposed to UV light. After a second bake, the plate was developed to remove any exposed photoresist. Aqua regia was used to etch any platinum that was not protected by photoresist and the subsequently exposed titanium was removed with titanium etchant (Transene Company Inc., Danvers, MA). The photoresist layer was then removed by acetone and the chip fabrication was finished by the addition of copper wire connections to the platinum electrodes. The copper wire was fixed with epoxy and the connection was made with colloidal silver (Ted Pella Inc., Redding, CA).

The chip is shown in Figure 1b. This chip had a variety of electrodes using a jagged-edge step to vary distance between electrodes of various sizes. A typical dual-electrode zoom is shown Figure 1c. The design enables us to vary the distance between the two working electrodes (W_f and W_r in Figure 1a) from $100\text{ }\mu\text{m}$ to 12 mm in $100\text{ }\mu\text{m}$ increments. In the experiments shown in this study the distance between the two working electrodes was 9.4 mm (unless otherwise noted).

2.3. Fluidics

The PDMS fluidic channels are created by soft photolithography using a negative photoresist. [25,29] A 100 mm silicon wafer was spin-coated with SU-8 50 photoresist to create a pattern ideally $100\text{ }\mu\text{m}$ in height. After a baking step, a negative mask of the desired fluidic channel dimensions was placed on the wafer and exposed to UV light. After a second bake the wafer was washed with 1-methoxy-2-propanol developer and isopropanol. To create a fluidic microchip from the silicon master, a mixture of 10:1 elastomer base and curing agent is poured onto the wafer with a high wall dam to enable a thicker layer. It is then allowed to cure in at $75\text{ }^{\circ}\text{C}$ oven for at least one hour. Once done, the channel is peeled and cut to size. A small hole is punched into one end with a 20 gauge luer stub adaptor, and a large hole is punched into the other end to act as a reservoir.

2.4. Cell Assembly

The PDMS channel was reversibly sealed over the electrode such that the rear electrode is at a specified distance to the center of the outlet reservoir. It has been shown that PDMS can be reversibly sealed to a variety of substrates, including glass, by a bringing the 2 surfaces into conformal contact. The channel network seals by van der Waals forces and is leak-free up to pressures of 5 psi. [36]

Near, intermediate, and distant reference/counter electrode placement designs were studied at distances of 2.4 mm, 5.7 mm, and 11.0 mm, respectively. (This distance is measured by the spacing between the reference/counter and the rear working electrodes.) A Harvard Apparatus microsyringe pump was used to pump the electrolyte into the system via 0.508 mm i.d. Tygon microbore tubing (New England Small Tube Corp, Litchfield, NH), through a steel pin that is simply inserted into the small hole created by the luer stub adaptor [37]. The channel is placed on top of the electrode. Fluid introduction is done by way of the steel pin through a hole in the PDMS layer, and the fluid exits into the channel reservoir on the other side of the working electrodes where the reference and counter electrodes both reside. An assembled device (without reference/counter electrodes) is shown in Figure 1d.

2.5. Procedures

After the cell was assembled, a solution of 0.5 M sulfuric acid was introduced to clean the electrode surface by 10–15 minutes of continuous cyclic voltammetry between -500 mV and 500 mV. The Pt surface was activated (in most of the experiments) with Bi^{3+} deposition [38] at -400 mV for 10 min. (The Bi^{3+} solution was prepared by dissolving Bi_2O_3 in 0.5 mol/L sulfuric acid; unless otherwise noted, 2×10^{-6} mol/L Bi^{3+} concentration was used). After cleaning and activation, the prepared solution of 1 mol/L formic acid and 0.5 mol/L sulfuric acid was loaded in the microsyringe. Polarization scan experiments were carried out with the software package of the potentiostat. Constant potential experiments were carried out by scanning the circuit potential (V) from open circuit (about -400 mV) to the target potential where the current data was saved at 200 Hz after discarding 20 seconds transients. The experiments were carried out at room temperature (21 ± 2 °C).

3. Results

3.1 Results for single electrodes

To validate the microfluidic setup, we investigated the dynamics of formic acid oxidation on a single electrode as a function of attached external resistance.

Without attached resistance a forward (slow) polarization scan is shown in Figure 2a. The system exhibits negative differential resistance (NDR) between $V = -0.07$ V and 0.355 V. This negative slope is due to OH poisoning of the direct path of formic acid oxidation. [5].

The negative differential resistance indicates that with enough uncompensated potential drop (IR drop) bistability/oscillations can be observed. [5] Figure 2b shows the bistability in forward and backward polarization scans with 200 k Ω external resistance. Between $V = 0.05$ V and 1.4 V the current is large on the forward but very small on the backward scan. These states are stable and exist even for very small scan rates and thus are not due to diffusional transients. At an even larger resistance of 10 M Ω (Figure 2c) oscillations occur on the forward scan between $V = 0.7$ V and 2.8 V. In the middle of the potential region at $V = 1.4$ V the oscillation waveforms are shown in Figure 2d; such oscillations can be observed for about 2–5 minutes after which the current of the electrode drops to a low value and the electrode is ‘poisoned’. After the cleaning procedure is repeated, the oscillations can be again reproduced.

The frequency and the phase of the current oscillations were determined with the Hilbert-transform method. [39–41] The method is illustrated in Figure 3 with current oscillations shown in Figure 2d. A two-dimensional embedding is constructed with the help of the Hilbert transform:

$$H(t) = 1/\pi \int_{-\infty}^{\infty} \frac{\tilde{i}(\tau)}{t - \tau} d\tau \quad (1)$$

where $\tilde{i}(t)$ is the current minus the mean current: $\tilde{i}(t) = i(t) - \langle i(t) \rangle$; $\langle \rangle$ denotes temporal mean. Figure 3a shows the two dimensional embedding $H(t)$ vs. $\tilde{i}(t)$. At each time t the phase $\varphi(t)$ is defined as the angle to the phase point in Figure 3a:

$$\varphi(t) = \arctan \frac{H(t)}{\tilde{i}(t)} \quad (2)$$

This definition can be applied to obtain phase if there exists a center of rotation in the phase space. Figure 3b shows the obtained (unwrapped) phase as function of time; the slope of curve 3.338 rad/s = 0.531 Hz gives the frequency of the oscillations. Although in figure 3b it is seen the phase is a linear function of time, a close inspection (figure 3c) indicates that there are quite large in-cycle fluctuations. These fluctuations are inherent in the applied phase definition but do not affect properties related to long term averaging such as frequency or phase diffusion coefficient. [39]

These experiments indicate that the dependence of observed dynamical behavior (NDR region without added resistance, bistability with small resistance, and oscillations with large resistance) on external resistance in microfluidic flow cell is similar to that observed in traditional macro-cells [30–32].

3.2 Results for dual electrodes

3.2.1. Distant reference electrode placement—The oscillatory formic acid oxidation on Pt dual electrodes was investigated with reference/counter electrode placement far away ($d = 11.0$ mm) from the rear Pt electrode. For comparison, we have carried out experiments with the front and rear electrodes separately. Figure 4a shows the current oscillations of the front electrode with 10 MΩ external resistance. The oscillations have a frequency of 0.439 Hz; the waveform exhibits some irregular variations that can be probably attributed to either temporal [30–32, 38] or spatio-temporal [42] instabilities. The rear electrode exhibited oscillation frequency and waveform different from those of the front electrode; these differences probably arise from somewhat different surface properties that develop during the deposition, cleaning, and activation procedures. With an external resistance of 12 MΩ, the oscillation waveform of the single rear electrode is shown in Figure 4b. (We applied an increased value of resistance for the rear electrode because at 10 MΩ the oscillatory frequency and waveform were quite different from those of the front electrode.) In contrast to the experiments with front electrode, the oscillations of rear electrode currents are very regular and have about 32 % larger frequency ($\omega = 0.581$ Hz).

When the front and rear electrodes were both polarized at the same time, some important changes occurred. As shown in figure 4c, the oscillations become synchronized; the frequencies of the oscillations of the two electrodes became equal (0.484 Hz) and the current peaks occurred at about the same time. The front electrode retained its irregular shape but due to the apparent interactions between the electrodes the behavior rear electrode became more irregular. For

example, at about 26.5 s there is current peak of the front electrode concurrent with a small negative current peak of the rear electrode; such negative current peaks of the rear electrode were not observed in the single-electrode experiment (Figure 4b).

The synchronization behavior can be illustrated by comparing the phase difference of the oscillations of the rear and front electrodes. Phase difference during the dual electrode experiment is shown in figure 4d. The phase difference is bounded and fluctuates around a mean value of -0.05 rad. The bounded phase difference indicates the presence of phase synchronization among the oscillations [39]; because the phase difference is small the oscillations are nearly in-phase. The relatively small, fast (roughly 0.5 Hz) in-cycle fluctuations of phase difference is due to small errors of phase definitions; such fluctuations have been observed in other synchronization experiments [40, 43] but, in general, does not affect long-term variation of phase differences.

We repeated the experiments with small working electrode ($500\text{ }\mu\text{m}$) spacing and observed that in-phase synchronization easily sets in when the inherent frequency of the individual oscillations were not very different. The most diverse electrodes that exhibited synchrony had oscillation frequencies of 0.8 Hz and 4.0 Hz with 2.5 Hz synchronized frequency. Occasionally, the synchronization set in with a frequency ratio in the range of 1:2 – 1:5 when the polarization curve of the two electrodes were quite dissimilar exhibiting oscillations onsets several hundred millivolts apart. An example is shown in figure 4e. 1:3 synchronization is observed; for every oscillations of the current of the front electrode there are three oscillations of the currents of the rear electrode.

Synchronization was not strongly affected by changes in flow rates in the range of $Q = 0\text{--}3\text{ }\mu\text{L}/\text{min}$. At larger flow rates, complicated, irregular oscillations were observed similar to those reported on macroelectrodes [30–32,38]; since these oscillations did not produce a unique center of rotation in the Hilbert phase the synchronization properties were difficult to evaluate.

3.2.2. Intermediate and near reference electrode placements—Figure 5a shows the results of a dual electrode experiment when the reference/counter electrodes were placed to about half of the distance ($d = 5.7\text{ mm}$) to the rear working electrode than in the example above ($d = 11.0\text{ mm}$). Synchronized oscillations were observed similar to those shown with distant reference electrode during the initial phase of the experiment ($10\text{ s} < t < 80\text{ s}$). However, for $t > 80\text{ s}$ the synchrony of the oscillations breaks down; the synchronized oscillations (that typically last for about four cycles) are interrupted by phase slips [39]. In the slipping region four oscillations of the front (fast) electrode are accompanied by three oscillations of the rear (slow) electrode. The synchronized and phase slipping regions alternate. These synchronization characteristics can also be seen, to a lesser extent, in the dynamics of phase differences (figure 5b). For ($10\text{ s} < t < 80\text{ s}$) the phases are locked and nearly in-phase synchronization can be observed. For $t > 80\text{ s}$ the phase difference increases with a slowing down at values close to multiples of 2π . (The 2π jumps in phase slipping is somewhat hindered by the large in-cycle fluctuations of phases.) Therefore, at the early phase of the experiment the coupling between the electrodes was strong enough to maintain synchrony; during the experiment, the inherent frequency of the oscillations drifted apart and the coupling between the electrodes was not strong enough to maintain synchrony. The observed phase dynamics during the experiment is an indication of weakened coupling between the electrodes due to the closer placement of reference electrode.

Dual electrode experiments were also carried with very close placement of the reference/counter electrode; the rear working electrode was about $800\text{ }\mu\text{m}$ apart from edge of the channel reservoir, therefore, the total reference electrode distance ($d = 2.4\text{ mm}$) was largely due to the size of the outlet channel reservoir. The current oscillations with this close reference electrode

placement exhibited no sign of synchrony. The oscillations are shown in figure 5c; the peaks do not line up in an obvious manner and the waveforms do not exhibit the 'negative' peak behavior typically seen with synchronized (or partially synchronized) oscillations. The frequencies of the front and rear electrodes were 0.595 Hz and 0.795 Hz, respectively. The rear oscillator was about 34 % faster than the front electrode; this frequency difference is comparable to that of the experiment with far electrode placement (32 %). However, the phases diverge linearly (see figure 5d) with the near placement of the reference electrode. The phase drift behavior is an indication of lack of coupling among the oscillators.

3.2.3. Coupling mechanism and strength—The synchronization experiments in dual electrode cells imply that negligible coupling exists with near reference/counter electrode placement; the coupling becomes relatively strong when the reference/counter electrodes are placed far away from the rear working electrode. We carried out independent experiments to evaluate the directionality and strength of the coupling between the electrodes.

Figure 6a shows an experiment in which the circuit potential of the front electrode is set to a value where oscillations occur while the circuit potential of the rear electrode is set to a sub-oscillatory value with near reference electrode placement. The sub-oscillatory potential is determined as the potential approximately 50 ± 25 mV below the onset of oscillations. It is seen that no induced ('driven') oscillations can be observed in the currents of the rear electrodes. Similarly when the rear electrode was oscillatory and the front electrode sub-oscillatory (figure 6b) there are no apparent oscillatory traces in the current of the front electrode. These experiments show that with near reference electrode placement the interactions between the electrodes are negligibly weak.

Similar experiments were carried with distant reference electrode placement. In contrast to the close reference electrode placement experiments, the oscillatory front electrode clearly drives the sub-oscillatory rear electrode (see figure 6c). The current of the rear electrode exhibits oscillations that follow that of the front electrode with an amplitude ratio of about 10 %. Similarly, current oscillations of the rear electrode are capable of driving the front electrode with an amplitude ratio of about 6 %. These experiments indicate that the coupling between the electrodes is bidirectional; the differences in the amplitude ratios are most likely due to the differences of the 'responsiveness' of the sub-oscillatory front and rear electrodes due to different surface conditions and circuit potential distance to the respective bifurcation points.

The dominant interaction among the electrodes is thus the bidirectional electric coupling; mass transfer interactions would be unidirectional from the front to the rear electrode and would not be affected by the reference electrode placement.

4. Discussion

The non-linear behavior investigated in this study is very sensitive to slight differences of surface conditions; these small heterogeneities result in differences of frequencies of the oscillations of electrodes. However, the oscillatory electro-oxidation on the two Pt electrodes became nearly in-phase synchronized when the reference/counter electrodes were placed sufficiently far away from the working electrodes. The in-phase synchrony has been seen in a large number of negative-differential resistance oscillators close to Hopf bifurcations due to positive electrical coupling [12,14,21]. Out-of-phase and anti-phase synchrony are typically contributed to negative coupling [16,44], the deformation of phase dynamics due to the relaxation character of the oscillators[44], or external (non-linear) feedback [45,46]. It is likely that these factors do not contribute significantly to the observed dynamics because our experiments indicated in-phase synchrony in the investigated parameter region. The experiments thus confirm the previous findings that negative differential electrochemical

oscillators have a tendency to synchronize in-phase with positive electrical coupling (close to a Hopf bifurcation).

In the microfluidic flow cell, the coupling between the electrodes can be either bidirectional through the potential drop in the cell or unidirectional through mass transfer from the front to the rear electrode. The experiments show that the reference/counter electrode placements strongly affect the synchronization properties; this indicates the importance of electric coupling. Synchronization occurred with distant reference electrode placement even when the two $120\text{ }\mu\text{m} \times 100\text{ }\mu\text{m} \times 0.2\text{ }\mu\text{m}$ electrodes were as far as 9.4 mm apart. The phase dynamics of the oscillations were not affected by coupling when the reference electrode was at the distance of 2.4 mm. The decrease of global, electric coupling strength with working to reference electrode placement has been interpreted theoretically [5,47] and demonstrated in synchronization of dual-electrode H_2O_2 reduction [21] and active-passive iron oscillations [15] in macro-cells. Therefore, when elimination of electric interaction is required, a near placement of counter/reference electrode is recommended. It is not uncommon to minimize working to counter/reference electrode distances in on-chip electroanalytical applications to decrease potential drop [48,49]; our studies indicate that distant placement also introduces electric coupling in cell geometries typically used for analytical purposes and thus should be avoided. It is possible to microfabricate cells with Pt counter electrode as close as a few μm with the lithography technique used in this study. (In this case the reference electrode still could be placed in the channel reservoir since there is only very small current/potential drop behind the counter electrode). It should be noted, however, that very close reference electrode placement might result in negative coupling [50].

We also showed that the dominance of electric coupling in dual-electrode experiments when the circuit potential values were set for one electrode in the oscillatory and the other electrode in the sub-oscillatory regions. With near reference/counter electrode placement, no driven current was seen for the sub-oscillatory electrode. In contrast, with distant reference electrode placement driven currents could be observed for both sub-oscillatory front and rear electrodes. The applied formic acid concentration (1 mol/L) and the small current (0.1 μA) probably contributes to the lack of effect of mass transfer interactions on oscillatory dynamics; the role of mass transfer interactions could be improved by varying inlet formic acid concentration and the electrode numbers/sizes/spacings. Future work will include the optimization of cell geometry for unidirectional mass transfer interactions.

The applied oscillatory-sub-oscillatory dual electrode experiment for exploring interactions is similar to calculating cross-impedance for the electrodes. However, instead of using an external sinusoidal potential signal to generate harmonic oscillations, we make use of inherent oscillations of the electrochemical reaction. There is a growing interest in nonlinear dynamics to explore topology/strength of interactions among units from dynamical data [51,52]; for example, such methods can help decrypting the wiring diagram of the brain. The developed experimental setup could serve a good test-bed for improving these reverse-engineering methodologies since the inherent dynamics of the particles and the interactions strength/topology can be easily controlled with cell design and chemical and mass transfer conditions.

5. Conclusions

The microfluidic dual-electrode flow cell provided a convenient way for investigating the spatial and temporal characteristics of formic acid electro-oxidation. The negative differential resistance of the electrochemical reaction produced bistable and oscillatory current behaviors in the on-chip electrochemical cell similar to those observed with macro-cells. [30–32] Although the experiments were carried out in single and dual electrode configurations, the extension to multi-electrode array setup is straightforward. Lithographic techniques provide

convenient ways for cell design with various array topologies (electrode size/spacing). The ability to reversibly seal the PDMS flow channel over the electrode array makes the investigation of spacings a relatively easy process. As can be seen in Figure 1c, if a different electrode spacing is desired the PDMS channel is simply peeled from the plate and re-sealed over the desired electrode pattern. The combination of on-chip electrode fabrication with microfluidic flow control enables the investigation of electrochemical processes that require well-defined flow control. Therefore, the controlled cell geometry and flow conditions could provide means for precise measurements in multi-electrode studies of importance in corrosion, bio-electrocatalysis, and fuel cells.

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Figure 1.

Experimental set-up. a) Schematic of dual-electrode flow cell. W_f , W_r , R, and C are front and rear working, reference, and counter electrodes, respectively. Arrow indicates flow of electrolyte. R_{ext} : external resistors. b) Glass round containing Pt electrodes of varying sizes (100 μm – 12 mm) and distances. c) Dual-Pt electrodes with PDMS-based flow channel. d) Assembled microfluidic dual-electrode flow cell (without reference and counter electrode)

Figure 2.

Polarization scans of formic acid electro-oxidation on single Pt electrode with various external resistances. a) Forward scan without added resistance. Scan rate, $\nu = 5 \text{ mV/s}$. $Q = 1.5 \text{ }\mu\text{L/min}$. b) Cyclic scan with $R_{\text{ext}} = 200 \text{ k}\Omega$. $\nu = 15 \text{ mV/s}$. $Q = 1.5 \text{ }\mu\text{L/min}$. c) Cyclic scan with $R_{\text{ext}} = 10 \text{ M}\Omega$. $\nu = 25 \text{ mV/s}$. $Q = 2.5 \text{ }\mu\text{L/min}$. d) Time series of current oscillations with $R_{\text{ext}} = 10 \text{ M}\Omega$, $V = 1.400 \text{ V}$. $Q = 2.5 \text{ }\mu\text{L/min}$. Arrows indicate scan directions. $c(\text{Bi}^{3+}) = 0 \text{ mol/L}$, $c(\text{HCOOH}) = 1 \text{ mol/L}$, $c(\text{H}_2\text{SO}_4) = 0.5 \text{ mol/L}$.

Figure 3. Phase definition current oscillations. a. Hilbert transform representation used for definition of phase. The square symbol indicates the center of rotation. b, Phase vs. time. c. Same as panel b with zoom to $15\text{ s} < t < 20\text{ s}$. The data (partially) shown in Figure 2d was used in this data analysis.

Figure 4.

Synchronization of current oscillations in dual electrode cell with far reference electrode placement ($d = 11.0$ mm). a) Time series of current oscillations of the (single) front working electrode. $\omega(\text{front}) = 0.439$ Hz. b) Time series of current oscillations of the (single) rear working electrode. $\omega(\text{rear}) = 0.581$ Hz. c) Synchronized current oscillations in the dual electrode setup. $\omega(\text{front}) = \omega(\text{rear}) = 0.485$ Hz. Solid line: front electrode, bold line: rear electrode. d) Phase difference between the oscillations of the rear and front electrodes vs. time in the dual electrode set-up. $Q = 1.5$ $\mu\text{L}/\text{min}$. Front electrode: $V = 1.2$ V, $R_{\text{ext}} = 10$ M Ω . Rear electrode: $V = 1.3$ V, $R_{\text{ext}} = 12$ M Ω . $c(\text{Bi}^{3+}) = 2 \times 10^{-6}$ mol/L. e. 1:3 synchronized current oscillations. $Q = 2$ $\mu\text{L}/\text{min}$.

$V = 0.8 \text{ V}$, $R_{\text{ext}} = 10 \text{ M}\Omega$. $c(\text{Bi}^{3+}) = 2 \times 10^{-7} \text{ mol/L}$. $c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol/L}$. $c(\text{HCOOH}) = 0.1 \text{ mol/L}$

Figure 5.

Current oscillations in dual electrode cell with medium ($d = 5.7$ mm, front row) and close ($d = 2.4$ mm, bottom row) reference electrode placements. Top row: Partially synchronized current oscillations in dual electrode with medium reference electrode placement. For both front and rear electrodes: $V = 0.8$ V, $R_{\text{ext}} = 10$ M Ω . Bottom row: Non-synchronized current oscillations in dual electrode with close reference electrode placement. For both front and rear electrodes: $V = 0.7$ V, $R_{\text{ext}} = 10$ M Ω . Left column: Current oscillations vs. time. Solid line: front electrode, bold line: rear electrode. Right column: phase difference. In panel b the dashed lines indicate changes of 2π phase differences. $Q = 1.5$ $\mu\text{L}/\text{min}$. $c(\text{Bi}^{3+}) = 2 \times 10^{-6}$ mol/L.

Figure 6.

Effect of current oscillation of one electrode on the sub-oscillatory behavior of the other electrode in dual electrode flow cell for near (panels a, b; $d = 2.4$ mm) and distant (panels c, d; $d = 11.0$ mm) reference electrode (RE) placements. In each panel the top and bottom plots are for front and rear electrodes, respectively. a) Oscillatory front and sub-oscillatory rear electrode for near RE placement, $V(\text{front}) = 0.700$ V, $V(\text{rear}) = 0.300$ V. b) Sub-oscillatory front and oscillatory rear electrode for near RE placement, $V(\text{front}) = 0.25$ V, $V(\text{rear}) = 0.700$ V. c) Oscillatory front and sub-oscillatory rear electrode for distant RE placement, $V(\text{front}) = 0.700$ V, $V(\text{rear}) = 0.350$ V. d) Sub-oscillatory front and oscillatory rear electrode for distant RE placement, $V(\text{front}) = 0.200$ V, $V(\text{rear}) = 0.700$ V. In all experiments $Q = 1.5$ $\mu\text{L}/\text{min}$ and $R_{\text{ext}} = 10$ M Ω .